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The spectra and structure of sulphur-containing organic compounds—II. The vibrational spectra and internal rotation of dimethylsulphate

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Abstract—An investigation of the i.r. spectra of $(CH_3O)_2SO_2$ in liquid and crystalline states has been carried out. The crystals were obtained by freezing the liquid and precipitating the vapour on a cooled KBr plate. Four crystalline modifications have been obtained. The i.r. spectra of oriented crystalline films have been investigated in polarized light. A normal coordinate analysis has been carried out, an interpretation of the spectrum given and the force field determined. It has been shown on the basis of experimental data and theoretical analysis that there is an equilibrium of three rotational isomers in $(CH_3O)_2SO_2$ in the liquid and solutions. Different numbers of conformers have been found in different crystalline modifications.

INTRODUCTION

In recent years we have been investigating the vibrational spectra and have been carrying out a conformation analysis of sulphur-containing compounds. The data on internal rotation about S–C [1–3] and S–O bonds [4] have been obtained. The rotational isomerism of dimethylsulphate (DMSA) has not been studied so far. The i.r. and Raman spectra of liquid DMSA and DMSA-d_6 were investigated in [5], spectra interpretation has been carried out on the basis of one isomer form.

The present paper presents an investigation of the i.r. spectra of liquid and crystalline DMSA and a normal coordinate analysis. An interpretation of the vibrational spectrum has been given and DMSA force field has been obtained. The conformation analysis of DMSA has been given much.

EXPERIMENTAL

The i.r. spectra were recorded and oriented crystalline films were grown in the same manner as in [4, 6]. The spraying of thin sample films (~ 0.01 mm thick) on a KBr plate cooled down to 80°K was carried out in a vacuum cryostat whose design is similar to the one described in [7]. Temperature was recorded with a copper-constantan thermocouple. Films of the necessary thickness were obtained in all the runs in the period of several seconds. Commercial DMSA purified by distillation was used.

RESULTS AND DISCUSSION

We have obtained the i.r. spectra of DMSA in liquid and crystalline states (Tables 1 and 2). The i.r. spectrum of the liquid is similar to the one presented in [5]. While growing crystals from the liquid two crystalline modifications of DMSA were obtained: crystal I and crystal II. Crystal I (Fig. 1(a)) was obtained by slow cooling of a thin liquid film to ~ 235 K. When the temperature was further decreased to ~ 203 K changes of all the spectrum parameters were observed testifying to the phase transition crystal I–crystal II. It was accompanied by frequency shifts, i.r. absorption band intensity changes, changes in band half-widths, disappearance of the 522 cm^{-1} band (Fig. 1, Table 2). The crystalline modifications obtained are enantiotropic: both polymorphous forms are stable over their temperature ranges and a reversible transition is possible between them.

When the temperature was lowered a decrease in the intensity of the 522, 558 and 778 cm^{-1} bands was observed in the liquid film spectrum whereas the intensity of the other bands was increased. These bands are retained in crystalline modification I (Fig. 1(a)). During the phase transition crystal I–crystal II the 522 cm^{-1} band was "frozen out". This was well observed in the investigation of crystalline films in polarized i.r. light (Fig. 1(b)).

Spectra of crystals obtained by a different method have also been investigated. For this purpose DMSA vapour was precipitated on a KBr plate cooled to 80 K, which was followed by annealing. In this way two new crystalline DMSA modifications were obtained: crystal *A* and crystal *B*. The solid film spectrum at 80 K prior to annealing is presented in Fig. 2(a) and in Table 2. An increase in the temperature of this film to ~ 173 K did not result in any appreciable variation of the i.r. spectrum. Sharp changes occurred in the spectrum at 173 K (band splittings, relative intensity and half-width changes) (Fig. 2(b), Table 2), which are characteristic of sample crystallization, and crystal *A* was formed. This crystalline modification is stable over the temperature range 80–~ 228 K. At ~ 228 K sharp changes again occurred in the spectrum, which accompanied the phase transition crystal *A*–crystal *B* (Fig. 2(c), Table 2). Further temperature variations in the range 80–242 K (melting point) did not result in appreciable changes in the i.r. absorption spectra.

* See Part I, A. B. REMIZOV, A. I. FISHMAN and I. S. POMINOV, *Spectrochim. Acta* 35A, 901 (1979).